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Synthesis and Characterization of *trans*-Dicyano-(1,4,8,11-Tetraazacyclotetradecane) Chromium(III) Perchlorate [1]

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Thermal and photochemical studies of chromium(III) complexes containing the macrocyclic tetradentate amine ligand cyclam (1,4,8,11-tetraazacyclotetradecane) have provided valuable mechanistic insight into the thermal and photosubstitution behavior of Cr(III) species [2, 3]. However, the range of *cis*- and *trans*-Cr(cyclam)(X)$_2^+$ complexes so far investigated (where X$^-$ is a unidentate anion) is rather limited, due in part to difficulty in devising satisfactory synthetic routes to the *trans*-isomers [4, 5]. This problem has been recently addressed by Poon and Pun [5]; they describe a procedure for isomerizing *cis*-Cr(cyclam)Cl$_2^+$ to *trans*-Cr(cyclam)Cl$_2^+$ and the latter's subsequent employment in the preparation of *trans*-Cr(cyclam)(NCS)$_2^+$. We report here a convenient high-yield synthetic route to the dicyano complex *trans*-Cr(cyclam)(CN)$_2^+$, and explore its potential use as a precursor to other *trans*-X$_2$ species. In a separate communication we will describe the unusual photochemical and photophysical properties of the dicyano complex [6].

Experimental

Reagents

The free ligand cyclam was purchased from Strem Chemicals, while CrCl$_3$·3THF was obtained from Alfa/Ventron. A *cis*/*trans* mixture of [Cr(cyclam)-Cl$_2$]Cl was prepared following the literature procedure [4]. The corresponding perchlorate salt was isolated by addition of NaClO$_4$ to a 40 °C aqueous solution of the *cis*/*trans* chloride salt. All other reagents were of analytical grade quality (Fisher Scientific), and were used without further purification.

Measurements

Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, and infrared data were collected on a Perkin-Elmer 283 spectrophotometer using KBr pellets. Conductance measurements in water were determined using a Markson Electromark Analyzer (Model 4403). Emission spectra were obtained using a modified 4-8203D Aminco-Bowman spectrophotofluorimeter equipped with a Hamamatsu 666 photomultiplier. Elemental analyses (C, H, N, Cl) were performed by Midwest Microlabs. Flame atomic absorption analysis on an Instrumentation laboratory 551 AA spectrophotometer was employed for percent Cr calculations, after sample oxidation in basic H$_2$O$_2$ to chromate ion.

Syntheses

trans-*[Cr(cyclam)(CN)$_2$]ClO$_4$*

A 1.50 g sample (2.4 × 10^{-4} mol) of *cis*/*trans*-[Cr(cyclam)Cl$_2$]ClO$_4$ was dissolved in 20 ml dimethylsulfoxide (Me$_2$SO). The solution was heated to 62 °C and finely ground NaCN (1.40 g, 2.9 × 10^{-2} mol) was added. The reaction mixture was magnetically stirred at 62 °C for 70 minutes, then cooled to room temperature. The yellow product was collected by suction filtration, washed with ethanol and ether, and air dried (1.60 g, approx. 100%). This crude product was purified by dissolving in a minimum volume of warm water (800 ml), filtering to remove a trace of green impurity, and adding excess solid NaClO$_4$ to the filtrate. The yellow precipitate was filtered off, washed with ethanol and ether, and suction dried (0.77 g, 1.9 × 10^{-3} mol; 54%). *Anal.* Calculated for CrC$_{12}$H$_{24}$N$_6$ClO$_4$: C, 35.69; H, 5.99; N, 20.81; Cl, 8.78; Cr, 12.88. Found: C, 35.94; H, 6.27; N, 20.16; Cl, 8.99; Cr, 12.75. *CAUTION*: Although we have encountered no safety problems with this compound, perchlorate salts of TM complexes should be handled with care.

trans-*[Cr(cyclam)(CN)$_2$]Cl*

A 300 mg sample (7.4 × 10^{-4} mol) of *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ was suspended in 20 ml water with 340 mg (7.6 × 10^{-4} mol) of tetraphenylarsonium chloride dihydrate. The mixture was magnetically stirred at 45 °C for 5 min, then filtered and washed with 3 ml water to remove insoluble tetraphenylarsonium perchlorate. The yellow-orange filtrate was concentrated to 5 ml by heating under an air-stream, and acetone added to precipitate the complex chloride salt. The product was filtered off, washed with acetone and ether, and suction dried (245 mg, 97%).

trans-*[Cr(cyclam)(NCS)$_2$]ClO$_4$*

A 230 mg sample (5.6 × 10^{-4} mol) of *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ was added to 7 ml 0.5 *M*

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TABLE I. UV–Visible Spectral Data for Cyano/Amine Cr(III) Complexes in Aqueous Solution.

Complex	λ_{max}[a]	Ref.
$Cr(NH_3)_6^{3+}$	463 (39.4); 351 (32.7)	7
$Cr(NH_3)_5CN^{2+}$	451 (42.6); 347 (37.7)	8
cis-$Cr(NH_3)_4(CN)_2^+$	436 (49.0); 342 (37.6)	9
trans-$Cr(NH_3)_4(CN)_2^+$	440 (42.6); 344 (41.5)	9
cis-$Cr(en)_2(CN)_2^+$	434 (69.5); 339 (62.2)	10, 11
trans-$Cr(en)_2(CN)_2^+$	433 (50.1); 337 (42.7)	11
trans-$Cr(cyclam)(CN)_2^+$	414 (62.5); 328 (62.5)[b]	this work
$Cr(CN)_6^{3-}$	377 (85.9); 307 (59.5)	12

[a] Absorption wavelengths in nm. Values in parentheses are the molar absorptivities. [b] The corresponding *minima* for *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ are 294 nm (22); 365 nm (22).

nitric acid, and the solution magnetically stirred at 84 °C for 1¾ h while maintaining constant volume with added water. The resultant orange solution of *trans*-$Cr(cyclam)(H_2O)_2^{3+}$ was filtered, and a large excess (4.0 g) of NaSCN added to the filtrate. After heating at 84 °C for 1¾ h the solution was cooled to room temperature. The orange solid obtained was collected, washed with 2 ml concentrated aqueous NaSCN solution, 2 ml ethanol/ether (1:4), ether, and suction dried (98 mg, 37%).

Results and Discussion

trans-*Cr(cyclam)(CN)*$_2^+$

Preparation

Although a very large range of acidoamine complexes of Cr(III) are known, relatively few examples of mixed cyanoamine species have been reported (see Table I). Synthetic problems associated with CN^- anation of Cr(III) amine complexes have been discussed by Riccieri and Zinato [8, 9]. Our efforts to synthesize the title compound via CN^- anation of $Cr(cyclam)(Me_2SO)_2^{3+}$ in Me_2SO solution were unsuccessful, despite the utility of this route for the corresponding *cis*- and *trans*-$Cr(NH_3)_4(CN)_2^+$ species [9]. However, a simple alternative route involving heating *cis/trans*$[Cr(cyclam)Cl_2]ClO_4$ with excess NaCN in Me_2SO solution proceeds smoothly yielding the *trans*-dicyano product in good yield. Initially this product was prepared using *trans*-$[Cr(cyclam)Cl_2]ClO_4$ as starting material. However, in an analogous synthesis using the more readily available *cis*-$[Cr(cyclam)Cl_2]ClO_4$, i.r. and u.v.–visible spectral data as well as acid hydrolysis evidence (*vide infra*) showed the dicyano product to again have the *trans* configuration. This observation indicates that CN^- nucleophilic substitution is accompanied by *cis* → *trans* isomerization. In subsequent experiments, therefore, the *cis/trans*-$[Cr(cyclam)Cl_2]ClO_4$ mixture obtained directly from the reaction of $CrCl_3 \cdot 3THF$ with cyclam was employed as starting reagent. The *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ product has a somewhat limited solubility in water and aprotic solvents, and may be readily converted to the more soluble chloride salt by treatment with tetraphenylarsonium chloride in aqueous solution. The chloride salt also provided convenient access to the corresponding bromide, iodide, and thiocyanate salts by addition of the appropriate sodium salt to aqueous solutions of *trans*-$[Cr(cyclam)(CN)_2]Cl$.

Characterization

The molar conductance of a 1×10^{-3} *M* aqueous solution of *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ (90 ohm^{-1} cm^2 mol^{-1}) compares favorably with the value of 92 reported for *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ [9], and is consistent with the expected 1:1 electrolyte status of the complex. The *trans* geometric configuration is assigned primarily on the basis of acid hydrolysis and i.r. data analysis. The complex is very inert to hydrolysis in neutral or alkaline solution, and more surprisingly is strongly resistant to acid hydrolysis. Whereas the half-life for loss of the first CN^- group for *trans*-$Cr(NH_3)_4(CN)_2^+$ is approximately one minute in 0.1 *M* acid at 25 °C [9], the corresponding value for the title compound is approximately four days [13]. However, complete cyanide hydrolysis occurs after heating near boiling for almost two hours in 0.5 *M* HNO_3 solution. The UV–visible spectra of the possible *cis*- and *trans*-$Cr(cyclam)(H_2O)_2^{3+}$ products have been reported previously [4], and differ markedly in both the energy and intensity of their absorption maxima. The spectrum of our aquated product matches very closely that of *trans*-$Cr(cyclam)(H_2O)_2^{3+}$ implying that the parent dicyano complex also has the *trans* configuration. This concluson assumes acid hydrolysis proceeds with retention of configuration – a result already observed for *cis*- and *trans*-$Cr(NH_3)_4(CN)_2^+$ and *cis*-$Cr(en)_2(CN)_2^+$ [10, 14], and in keeping with the well-documented stereorigidity of acid hydrolysis for Cr(III) complexes in aqueous solution [15].

The use of i.r. spectroscopy for *cis–trans* isomeric discrimination has been explored extensively by Poon and co-workers [5, 16, 17] for a variety of cyclam complexes. They report diagnostic distinctions between *cis* and *trans* isomers in the 790–910 cm^{-1} region. *Trans* complexes are characterized by two groups of bands – one band (often a doublet) near 890 cm^{-1} due primarily to the secondary amine vibration, and a singlet near 810 cm^{-1} arising predominantly from the methylene vibrations. The corresponding region for *cis* species displays considerably more splitting. The i.r. spectrum for our dicyano product shows a doublet at 882, 873 cm^{-1}, and a singlet at 800 cm^{-1} characteristic of the *trans* isomer. The cyanide ligand C≡N stretch appears at 2090 cm^{-1} as a weak singlet, providing further support (although limited) for a *trans*-dicyano geometry. The analogous C≡N stretch for *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ is reported at 2130 cm^{-1}. The significantly lower frequency for the cyclam complex indicates that the cyanide ligand is a better π-acceptor in the latter species, consistent with the macrocycle being a stronger σ *donor* than NH_3. The uv-visible spectrum of *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ (Table I) exhibits bands at 414 nm and 328 nm assigned as the ligand-field (LF) transitions of $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ parentage, respectively. The wavelength of the first LF band (414 nm) is substantially lower than that of *trans*-$Cr(NH_3)_4(CN)_2^+$ (440 nm) and *trans*-$Cr(en)_2(CN)_2^+$ (433 nm, see Table I), providing additional support for the higher σ donor strength of cyclam relative to NH_3. As previously found by Riccieri and Zinato for *cis*- and *trans*-$Cr(NH_3)_4(CN)_2^+$ [9], the LF spectrum of the title compound provides little geometrical information.

The new dicyano complex displays perhaps the most unusual photobehavior in room temperature solution of any Cr(III) species previously reported [6]. It displays no discernible photochemical reactivity, and exhibits an exceptionally strong, long-lived (340 μs) $^2E_g \rightarrow {}^4B_{1g}$ phosphorescence centered at 720 nm in aqueous solution. Furthermore, deuteration of the cyclam N–H protons results in a five-fold increase in the intensity and lifetime of the emission. The significance of this photobehavior will be discussed elsewhere [6].

Preparation of trans-*Cr(cyclam)(NCS)*$_2^+$

In an effort to develop a convenient, relatively general route to *trans*-$Cr(cyclam)X_2^+$ species we have investigated the acid hydrolysis of *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ followed by NCS^- anation. The procedure has proven reliable, employs a readily available *trans*-parent, and yields the *trans*-$[Cr(cyclam)(NCS)_2]ClO_4$ product in reasonable yield (37%). The *trans* geometry for the thiocyanato complex was verified by comparison of our u.v.–visible and i.r. spectral data with those reported by Poon and Pun [5]. An additional probe of geometric configuration is the $^2E_g \rightarrow {}^4B_{1g}$ phosphorescence lifetime in air-saturated, room temperature aqueous solution (*trans* 90 μs; *cis* 8 μs).

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